AFML-TR-79-4149
ADA078954

STRUCTURE MODIFICATION OF FLUOROCARBON ETHER BIBENZOXAZOLE POLYMERS TO IMPROVE HYDROLYTIC STABILITY

Polymer Branch

Nonmetallic Materials Division

October 1979

TECHNICAL REPORT AFML-TR-79-4149

Final Report for Period June 1975 to May 1978

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

ROBERT C. EVERS
Project Monitor

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER

J. M. KELBLE, Chief
Nonmetallic Materials Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFML/MBP, W-PAFB, OH 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AIR FORCE/56780/14 December 1979 — 110

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFML-TR-79-4149	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE *(and Subtitle)*: Structure Modification of Fluorocarbon Ether Bibenzoxazole Polymers to Improve Hydrolytic Stability	5. TYPE OF REPORT & PERIOD COVERED: Final Technical Report June 1975 - May 1978
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): R. C. Evers, G. J. Moore, J. L. Burkett	8. CONTRACT OR GRANT NUMBER(s): F33615-75-C-5095
9. PERFORMING ORGANIZATION NAME AND ADDRESS: See Block 18	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 24190402
11. CONTROLLING OFFICE NAME AND ADDRESS: Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson AFB, OH 45433	12. REPORT DATE: October 1979
	13. NUMBER OF PAGES: 37
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)*: Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson AFB, OH 45433

University of Dayton
Research Institute
300 College Park Avenue
Dayton, Ohio 45469

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Polymer
Bibenzoxazole
Fluorocarbon
Elastomer
Stability
Hydrolysis

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Hydrolytically and thermooxidatively stable fluorocarbon ether bibenzoxazole (FEB) polymers were synthesized by the acetic acid-promoted polycyclocondensation of fluorocarbon ether bis(o-aminophenol) monomers with novel fluorocarbon ether dithioimidate ester monomers. The dithioimidate esters were derived from hexafluoropropylene oxide (HFPO) or, preferably, from a combination of tetrafluoroethylene oxide (TFEO) and HFPO. The latter class of TFEO:HFPO-derived dithioimidate esters was tailored to impart improved hydrolytic

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

stability to the resultant FEB polymers while minimizing undesirable, concomitant increases in polymer glass transition temperatures (Tg). The polymers were obtained in moderate-to-high molecular weight and exhibited inherent viscosities in the range of 0.20 to 0.41 dl/g. Polymer structures were verified by elemental and infrared spectral analysis. Lower polymer Tg's were obtained with increased fluorocarbon ether content, a minimum value of -48°C (-55°F) being achieved. High thermooxidative stability of the HFPO- and TFEO:HFPO-based FEB polymers was substantiated by thermogravimetric analysis and isothermal aging studies in air. After isothermal aging in air for 200 hours at 288°C (550°F) and 260°C (500°F), representative polymers exhibited weight losses of 17 and 7 percent, respectively. Hydrolytic stability of the polymers was evaluated by exposure to a 95 percent relative humidity, 93°C (200°F) environment for prolonged periods of time. Based on comparative polymer Tg, inherent viscosity and infrared spectral data, the HFPO- and TFEO:HFPO-based FEB polymers exhibited vastly improved hydrolytic stability over analogous TFEO-based FEB polymers. Optimum hydrolytic stability and low temperature viscoelastic properties were achieved through the use of a TFEO:HFPO-derived dithioimidate ester synthesized by a reaction sequence specifically selected to eliminate formation of structural isomers which would lead to sites of hydrolytic instability in the polymer backbone. Based on these encouraging results, hydrolytically and thermooxidatively stable FEB polymers appear to have great potential for broad use temperature range elastomer applications which cannot be adequately met by current state-of-the-art materials.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project/Task Nr 2419/04, Work Unit Directive 24190402, "Polymers for Broader Temperature Fluid Containment Materials." It was administered under the direction of Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. R. C. Evers as the AFML Project Scientist. Co-authors were Dr. R. C. Evers and Mr. G. J. Moore (AFML/MBP), and Mr. J. L. Burkett, University of Dayton Research Institute (Contract Nr 33615-75-C-5095).

This report covers work conducted from June 1975 to May 1978. This manuscript was submitted by the authors in February 1979 for publication as a technical report.

The authors wish to thank Dr. T. Abraham for contributions in the synthesis operations and Dr. I. J. Goldfarb and Mr. E. J. Soloski for the thermal stability data. The Analytical Branch, Air Force Materials Laboratory, contributed the elemental analysis and mass spectral data.

TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	DISCUSSION	5
	1. Monomer Synthesis	5
	2. Polymer Synthesis	8
	3. Polymer Characterization and Evaluation	12
	4. Conclusions	18
III	EXPERIMENTAL	20
	1. Preparation of Solvents and Intermediates	20
	2. Preparation of Monomers	20
	3. Preparation of Polymers	23
	REFERENCES	24

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1.	Infrared Spectrum of TFEO:HFPO-Based Polymer (Trial Nr 5) (Film)	25
2.	TGA Curve of HFPO-Based Polymer (Trial Nr 4) in Air ($\Delta T = 20^{o}C/min$)	26
3.	Isothermal Aging Curves of HFPO-Based Polymer (Trial Nr 4) in Air	27
4.	Isothermal Aging Curves of TFEO:HFPO-Based Polymer (Trial Nr 5) in Air	28
5.	Infrared Spectrum of TFEO-Based Polymer (Film)	29
6.	Infrared Spectra of TFEO-Based Polymer After Exposure to 95% R.H., $93^{o}C(200^{o}F)$ Environment (Film)	30

LIST OF TABLES

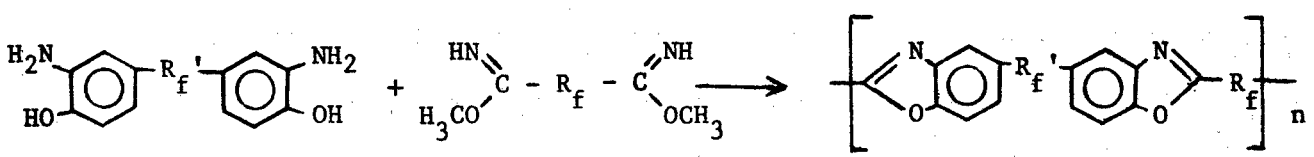
TABLE		
I	Characterization of Dithioimidate Ester Monomers	7
II	Preparation and Properties of HFPO-Based Polymers	9
III	Preparation and Properties of TFEO:HFPO-Based Polymers	10
IV	Comparison of Polymer Tg's	16
V	Hydrolysis Tests at 95% Relative Humidity and $93^{o}C$ ($200^{o}F$)	17

SECTION I

INTRODUCTION

The need for new thermooxidatively stable polymers as base materials for various Air Force seal applications has existed for some time. In order to satisfy the requirements anticipated for fluid containment in advanced cruise missles and aircraft, materials are needed which retain elastomeric properties over a -65 to 600°F temperature range. In addition, these materials must also exhibit other desirable properties such as hydrolytic stability, fluid resistance, mechanical strength, etc. over this temperature range. Since present state-of-the-art elastomers do not meet these broad use temperature range requirements, continuing research efforts to synthesize new polymer systems with inherently broader use temperature ranges have been carried on under both inhouse and contractual research programs.

In an earlier phase of an AFML inhouse research program (References 1-5), the synthesis of a series of novel, thermooxidatively stable fluorocarbon ether bibenzoxazole (FEB) polymers was achieved by the acetic acid-promoted polycondensation of novel fluorocarbon ether bis(o-aminophenol) monomers with long-chain fluorocarbon ether diimidate esters derived from tetrafluoroethylene oxide (TFEO).



$R_f' = (CF_2)_2O(CF_2)_5O(CF_2)_2$, $(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$, etc.

$R_f = CF_2(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF_2$, etc.

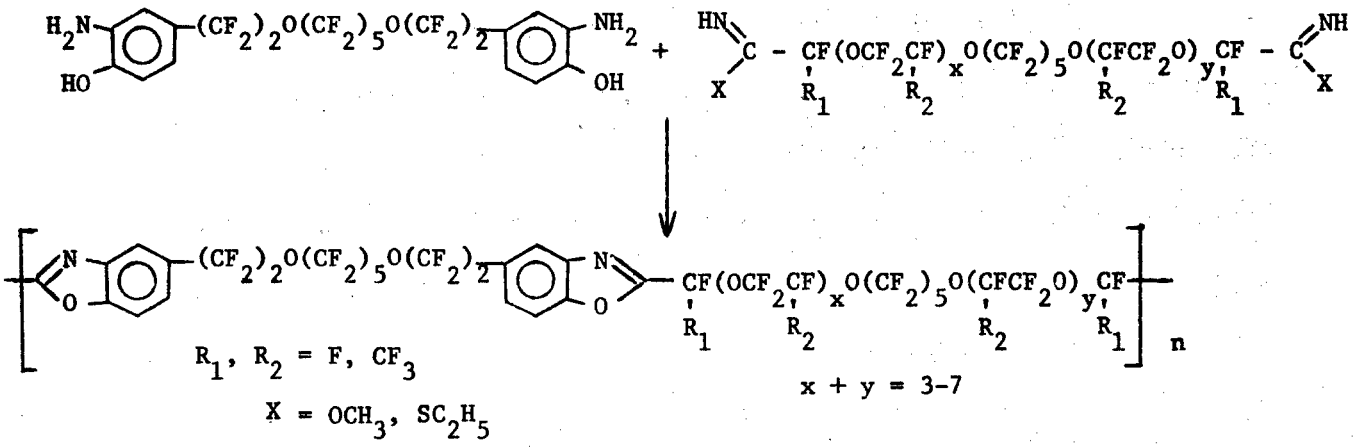
$x + y = 3\text{-}7$

This work was a follow-on to the initial phase of the inhouse program (References 6-9) and the research of Madison and Burton (References 10-16) but represented a significant advance over the earlier efforts in light of the drastically improved low temperature viscoelastic properties which were achieved without significant loss of thermooxidative stability. Through judicious choice of monomers and reaction conditions, moderate-to-high molecular weight FEB polymers with glass transition temperatures (Tg) as low as -58°C (-72°F) were obtained.

The above data strongly indicated great potential for achieving broader use temperature ranges for the FEB polymers than currently available in present state-of-the-art elastomers. However, additional data demonstrated that the FEB polymers were susceptible to hydrolysis as evidenced by deterioration of polymer samples upon exposure to high humidity at elevated temperatures. In order for these polymers to exhibit and maintain adequate mechanical properties under projected severe environmental conditions which include exposure to moisture at high temperatures, the problem of hydrolytic stability needed to be addressed and subsequent modification of the FEB polymer structure carried out.

Based on theoretical considerations and prior hydrolytic stability studies on fluorocarbon ether benzoxazole model compounds (References 17,18), FEB polymers synthesized from diimidate esters (R_1,R_2=CF_3;X=OCH_3) derived from hexafluoropropylene oxide (HFPO) would be expected to exhibit significantly improved hydrolytic stability along with increased Tg's over FEB

polymers previously synthesized from analogous TFEO-derived diimidate ester monomers (R_1,R_2=F; X=OCH_3).



The improved resistance to hydrolysis of the HFPO-based polymers would be attributable to the increased hydrolytic stability of the benzoxazole rings resulting from the shielding effect of the neighboring trifluoromethyl substituents (R_1=CF_3). FEB polymers synthesized from hybrid fluorocarbon ether diimidate esters (R_1=CF_3, R_2=F; X=OCH_3) derived primarily from TFEO (for maximum chain flexibility) but end-capped with HFPO (for hydrolytic stability) would also be expected to exhibit improved hydrolytic stability but with minimal increase in polymer Tg. The stiffening effect of the relatively bulky trifluoromethyl substituents on the polymer chain and the consequent undesirable increase in polymer Tg would be less pronounced in these TFEO:HFPO-based polymers because of the fewer trifluoromethyl substituents on the polymer backbone.

Previous attempts (Reference 6) to synthesize FEB polymers from HFPO-derived diimidate esters were unsuccessful and marked by the formation of blood-red reaction mixtures and extensive etching of the reaction flasks. Although variations in reaction conditions (solvent, temperature, etc.) were employed, the low molecular weight polymers isolated were dark-colored oils whose infrared spectra were not entirely consistent with the FEB polymer structure. Initial prototype polycondensation reactions indicated, however, that the analogous dithioimidate esters ($R_1,R_2=CF_3;X=SC_2H_5$) would react smoothly and cleanly with fluorocarbon ether bis(o-aminophenol) monomers to give HFPO-based FEB polymers in higher molecular weights.

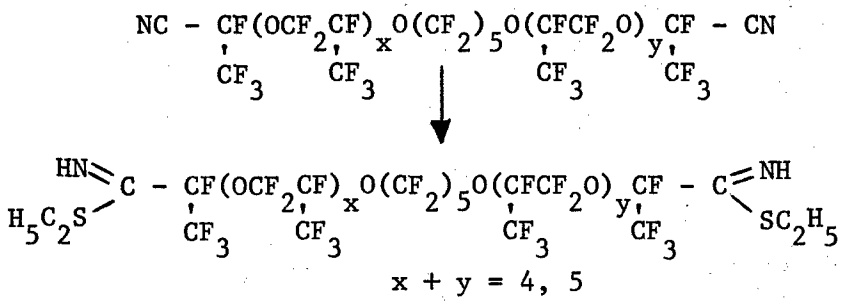
Accordingly HFPO- and TFEO:HFPO-derived dithioimidate ester monomers were synthesized and subjected to polycondensation reactions with known (References 1-3,5-7) fluorocarbon ether bis(o-aminophenol) monomers. The monomer syntheses as well as the subsequent FEB polymer syntheses and characterization are discussed in the following sections.

SECTION II

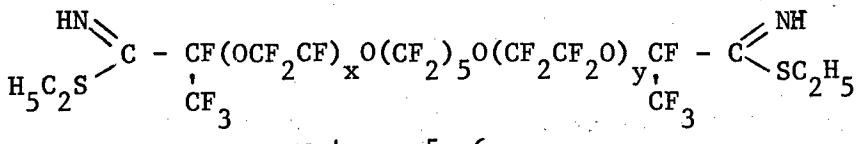
DISCUSSION

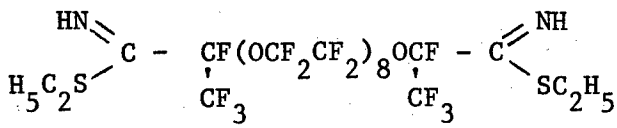
1. MONOMER SYNTHESIS

The HFPO-derived dithioimidate ester monomers were synthesized by the triethyl amine-catalyzed addition of ethanethiol to the corresponding fluorocarbon ether dinitriles. They were obtained in yields of 50-67%

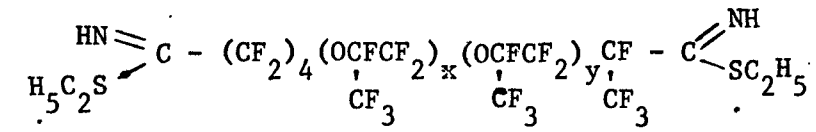


as clear, viscous liquids which had a distinctly unpleasant, persistent odor. Also synthesized in moderate yield by the same method were TFEO:HFPO-derived fluorocarbon ether dithioimidate esters.



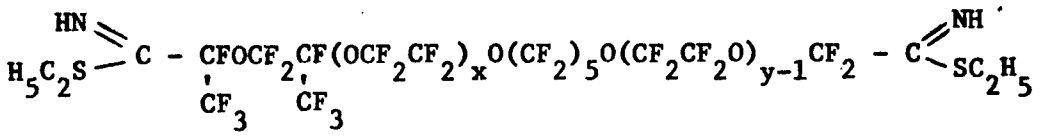


Because of the complexity of the synthetic reaction sequence used to obtain the precursor dinitriles (References 19,20), the presence of isomeric impurities in the dinitriles was suspected but could not be definitely ascertained because of the complex chemical structures. These impurities would be expected to be carried through the dithioimidate ester syntheses to give indeterminate quantities of inseparable, isomeric structures; e.g.,

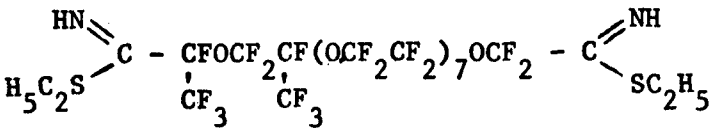


$$x + y = 4, 5$$

in the case of the HFPO-derived dithioimidate esters and



$$x + y = 5, 6$$



in the case of the TFEO:HFPO-derived dithioimidate ester monomers. Incorporation of these isomeric, unsymmetrical structures into the FEB polymer backbone during the subsequent polycondensation reaction would give rise to hydrolytically unstable structural imperfections; i.e., benzoxazole rings lacking the necessary shielding effect of the trifluoromethyl substituents. In order to synthesize a pure, non-isomeric

TABLE I

CHARACTERIZATION OF DITHIOMIDATE ESTER MONOMERS

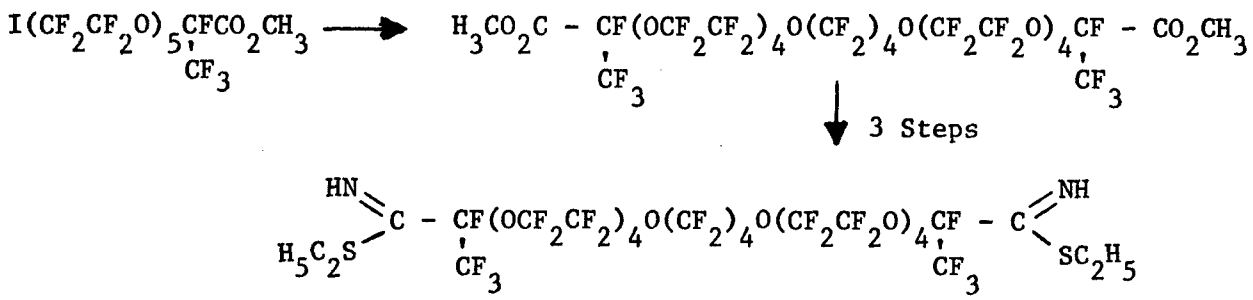
R_f'	Yield-%[a]	BP - °C	MW $\frac{\text{calc'd}}{\text{(found)}}$[b]	Analysis $\frac{\text{calc'd}}{\text{(found)}}$ C	H	N	S
$CF(OCF_2CF)_xO(CF_2)_5O(CFCF_2O)_yCF$ with CF_3 and CF_3 and CF_3 and CF_3; x + y = 4	67	147-50 / 0.02 mm Hg	1322 / (c)	24.52 / (24.42)	0.92 / (0.63)	2.12 / (2.13)	4.85 / (4.00)
" ; x + y = 5	50	168-72 / 0.03 mm Hg	1488 / (1488)	24.21 / (24.38)	0.81 / (0.75)	1.88 / (1.76)	4.31 / (4.72)
$CF(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF$ with CF_3 and CF_3; x + y = 5	61	152-53 / 0.05 mm Hg	1238 / (1238)	24.25 / (24.46)	0.98 / (0.98)	2.26 / (2.76)	5.18 / (5.13)
" ; x + y = 6	82	164-67 / 0.05 mm Hg	1354 / (1354)	23.94 / (23.93)	0.89 / (0.68)	2.07 / (2.20)	4.73 / (4.59)
$CF(OCF_2CF_2)_8OCF$ with CF_3 and CF_3	81	146-49 / 0.03 mm Hg	1320 / (1320)	23.65 / (23.75)	0.92 / (0.65)	2.12 / (2.01)	4.85 / (4.71)
$CF(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF$ with CF_3 and CF_3	80	178-80 / 0.40 mm Hg	1536 / (c)	23.54 / (23.61)	0.78 / (0.58)	1.82 / (1.81)	4.17 / (4.31)

(a) Based on the corresponding dinitrile.

(b) Mass spectroscopy.

(c) Parent ion peak was not always observed but fragmentation patterns supported the proposed structures.

TFEO:HFPO-derived dithioimidate ester monomer and thus eliminate potential sites of hydrolytic instability in the FEB polymers, a multistep reaction sequence based on the zinc-promoted coupling of a pure α,ω-fluorocarbon ether iodoester (Reference 21) was carried out. The symmetrical fluorocarbon ether diester product was converted via the diamide to the corresponding dinitrile. Subsequent reaction with ethanethiol in the presence of triethylamine gave pure dithioimidate ester monomer in 35% overall yield.



The intermediates and monomers were characterized by elemental analysis, infrared spectroscopy, and mass spectroscopy. The elemental analyses and physical constants of the new monomers are given in Table I.

2. POLYMER SYNTHESIS

Initial polymer synthesis efforts centered on the polycondensation of the HFPO-derived dithioimidate esters with known fluorocarbon ether bis(o-aminophenol) monomers (References 1-3,5-7). The reaction conditions and the properties of the HFPO-based FEB polymers are summarized in Table II.

TABLE II

PREPARATION AND PROPERTIES OF HFPO-BASED POLYMERS

Trial Nr	R_f'	R_f	Time-Hours	Concentration-% monomer $(\frac{w}{v})$	η_{inh} (a) dl/g	Tg-°C (b)	Analysis - calc'd (found) C	H	N
1	$(CF_2)_2O(CF_2)_2O(CF_2)_2$	$CF(OCF_2CF)_xO(CF_2)_5O(CFCF_2O)_yCF$ with CF_3 CF_3 CF_3 CF_3; $x + y = 4$	252	26	0.20	-15	28.76 (28.62)	0.35 (0.16)	1.64 (1.77)
2	"	" $x + y = 5$	192	37	0.20	-18	28.13 (27.92)	0.32 (0.14)	1.49 (1.51)
3	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	" $x + y = 4$	252	46	0.23	-19	28.38 (28.39)	0.32 (0.10)	1.50 (1.30)
4	"	" $x + y = 5$	240	36	0.25	-23	27.83 (27.57)	0.30 (0.25)	1.38 (1.40)
5	$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$	" $x + y = 5$	288	40	0.35	-34	27.10 (27.08)	0.27 (0.10)	1.24 (1.23)

(a) 0.2 g/dl, 25°C, HFIP.

(b) Differential Scanning Calorimetry ($\Delta T = 20°C/min$).

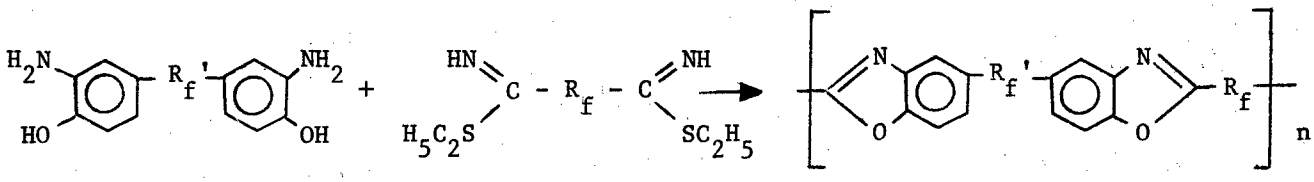
TABLE III

PREPARATION AND PROPERTIES OF TFEO:HFPO - BASED POLYMERS

Trial Nr	R_f'	R_f	Time-Hours	Concentration-% monomer $(\frac{w}{v})$	(a) η_{inh}-dl/g	(b) Tg-°C	Analysis - calc'd (found) C	H	N
1	$(CF_2)_2O(CF_2)_2O(CF_2)_2$	$CF(OCF_2CF_2)_8OCF$ CF_3 CF_3	456	36.0	0.27	-39	28.09 (28.22)	0.35 (0.08)	1.64 (1.75)
2	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$CF(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF$ CF_3 CF_3 $x + y = 5$	312	96.5	0.27	-35	28.37 (28.10)	0.34 (0.19)	1.57 (2.00)
3	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$CF(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF$ CF_3 CF_3 $x + y = 6$	336	60.0	0.41	-38	27.90 (27.98)	0.32 (0.02)	1.48 (1.67)
4	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$CF(OCF_2CF_2)_8OCF$ CF_3 CF_3	288	50.5	0.30	-37	27.76 (27.95)	0.33 (0.03)	1.51 (1.65)
5	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$CF(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF$ CF_3 CF_3	672	49.1	0.29	-45	27.19 (27.52)	0.29 (0.02)	1.35 (1.45)
6	$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$	$CF(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF$ CF_3 CF_3 $x + y = 6$	264	38.5	0.25	-44	27.79 (27.25)	0.28 (0.13)	1.54 (1.54)
7	$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$	$CF(OCF_2CF_2)_8OCF$ CF_3 CF_3	384	56.5	0.40	-47	26.98 (27.05	0.29 (0.12)	1.34 (1.44)
8	$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$	$CF(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF$ CF_3 CF_3	336	15.5	0.21	-48	26.54 (26.47)	0.26 (0.04)	1.21 (1.14)

(a) 0.2 g/dl, 25°C, HFIP.

(b) Differential Scanning Calorimetry ($\Delta T = 20°C/min$).



$R_f' = (CF_2)_2O(CF_2)_2O(CF_2)_2$

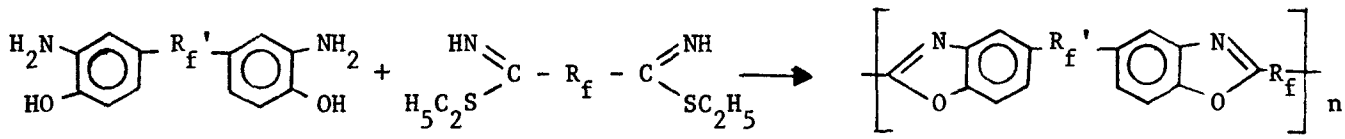
$(CF_2)_2O(CF_2)_5O(CF_2)_2$

$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$

$R_f = CF(OCF_2CF)_xO(CF_2)_5O(CFCF_2O)_yCF$ (CF_3 groups)

$x + y = 4, 5$

As in the previous polymer syntheses (References 1-9), the polycondensation reactions were run in hexafluoroisopropanol (HFIP) at moderate temperatures (50-55°C) for extended periods of time (8-12 days) and in the presence of approximately four molar equivalents of glacial acetic acid. High monomer to solvent concentrations of 25-50% (w/v) were used to minimize intramolecular reaction of the growing polymer chains and suppress formation of macrocyclic compounds. The polycondensation reaction mixtures were homogeneous from the start and became increasingly viscous as the reactions progressed. Rubbery, amber-colored gums which exhibited inherent viscosities in the range of 0.20 - 0.35 dl/g were obtained in yields of 70-80%.



$R_f' = (CF_2)_2O(CF_2)_2O(CF_2)_2$

$(CF_2)_2O(CF_2)_5O(CF_2)_2$

$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$

$R_f = CF(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF$, CF_3, CF

$x + y = 5, 6$

$CF(OCF_2CF_2)_8OCF$, CF_3, CF_3

$CF(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF$, CF_3, CF_3

Polycondensation reactions of the TFEO:HFPO-derived dithioimidate ester monomers with fluorocarbon ether bis(o-aminophenol) monomers were carried out in a similar manner although higher reaction concentrations and longer reaction times were generally used. Inherent viscosities in the range of 0.21 to 0.41 dl/g were recorded. The reaction conditions along with the resultant polymer properties are summarized in Table III.

3. POLYMER CHARACTERIZATION AND EVALUATION

The FEB polymers synthesized under this phase of the research program were clear, amber-colored gums of varying toughness depending upon the polymer molecular weight and Tg. All of the polymer samples were completely soluble in HFIP or Freon 113 but appeared to be completely unaffected by hydrocarbon-based solvents.

Polymer structures were established by elemental analysis and comparisons of infrared absorption characteristics with previously-synthesized model compounds and FEB polymers (References 4,6,7). Elemental analysis values of the polymer samples are given in Tables II and III and a representative infrared spectrum is shown in Figure 1. Present in the spectra in all cases were bands at approximately 1620, 1570, 1430, 1350, and 1300 cm^{-1} as well as the expected very strong absorptions in the 1100-1250 cm^{-1} region, attributable to the C-F stretching vibrations (Reference 22). No absorptions indicative of incomplete reaction and/or side-reactions were observed in the 1650-1800 and 3000-3500 cm^{-1} regions.

Thermooxidative stability of the polymers was evaluated by thermogravimetric analysis (TGA) and isothermal aging under an air atmosphere. Based on these thermal characterization methods, breakdown of the HFPO- and TFEO:HFPO-based polymers was approximately the same as previously observed with analogous TFEO-based polymers (References 1,5). Initial weight loss observed under TGA in air occurred at approximately 280°C (536°F) with a three % weight loss being recorded at 400°C (752°F). Weight loss was complete at 500°C (932°F). A representative TGA curve is shown in Figure 2. Isothermal aging in air of an HFPO-based FEB polymer and a TFEO-HFPO FEB polymer indicated fair thermooxidative stability at 288°C (550°F); 14 and 17% weight losses, respectively, were observed after 200 hours. However, both polymers exhibited very good thermooxidative stability at 260°C (500°F); weight losses of only 7% were observed. Isothermal aging curves are shown in Figures 3 and 4.

The Tg's of the HFPO- and TFEO:HFPO-based FEB polymers were determined by differential scanning calorimetry and are given in Tables II and III. As expected, lower Tg values were observed as fluorocarbon ether content increased; minimum Tg's of -34 and -48°C were recorded for the HFPO- and TFEO:HFPO-based polymers, respectively. No crystallinity was detected in any of the polymer samples. As expected, the Tg's of the HFPO-based polymers were appreciably higher than those recorded for the TFEO-based FEB polymers (References 1-5). The trifluoromethyl substituents in the HFPO-based polymers reduced the flexibility of the polymer chains and thus led to higher polymer Tg's. Comparisons between similarly structured HFPO-based polymers and TFEO-based polymers can be seen in Table IV (Example Nrs. 1,2). However, the Tg's of the TFEO:HFPO-based polymers, while not as low as those of the TFEO-based polymers, were significantly lower than the Tg's of the HFPO-based polymers. The differences in polymer Tg was a function of the relative TFEO and HFPO content in the polymer backbones. The minimal HFPO content in the TFEO:HFPO-based polymers gave rise to Tg's lower than observed in the HFPO-based polymers. A comparison between analogous TFEO-, HFPO-, and TFEO:HFPO-based FEB polymers can be seen in Table IV (Example Nr. 3).

Relative hydrolytic stabilities of the HFPO- and TFEO:HFPO-based FEB polymers compared to the TFEO-based polymers were evaluated by exposure to a 95% relative humidity, 93°C (200°F) environment for time periods of up to 1010 hours. Comparisons were made of polymer infrared spectra absorptions, Tg's, and inherent viscosities at the beginning and

end of the tests. These results are summarized in Table V. The TFEO-based polymers (Test Nrs. 1,2) underwent extensive degradation from amber gums to dark-colored greases after 364 hours. Infrared spectra of a TFEO-based polymer before and after exposure to the high humidity environment (Test Nr. 1) are shown in Figures 5 and 6, respectively. Evidence of hydrolysis was observed in the infrared spectra after only 48 hours with the appearance of strong absorptions at 1710 and 1740 cm^{-1}. These are indicative of the formation of carbonyl groups resulting from hydrolysis of unshielded benzoxazole rings (Reference 22). The infrared spectra and Tg of the HFPO-based polymers were essentially unchanged after 654 hours (Test Nrs. 3, 4). Slight, possibly insignificant decreases in the inherent viscosities of these gums were noted. An FEB polymer synthesized from a TFEO:HFPO-derived dithioimidate ester monomer believed to contain isomeric impurities exhibited a slight increase in the infrared spectra absorption at 1740 cm^{-1} (Test Nr. 5). This infrared spectral change in conjunction with the slight decrease in polymer inherent viscosity was possibly indicative of limited hydrolysis attributable to hydrolytically labile sites in the polymer chain which resulted from the aforementioned unsymmetrical isomeric impurities. On the other hand, a TFEO:HFPO-based FEB polymer synthesized from the pure TFEO:HFPO-derived dithioimidate ester monomer did not exhibit any infrared spectral changes although slight changes in polymer inherent viscosity and Tg were noted (Test Nr. 6). Further, only with this polymer was the aluminum test container unetched. This evidence indicated the absence of hydrogen fluoride elimination during the hydrolysis test

TABLE IV

COMPARISON OF POLYMER TG'S

Example Nr	R_f'	R_f	η_{inh}- dl/g	Tg-°C
	$(CF_2)_2O(CF_2)_2O(CF_2)_2$	$CF(OCF_2CF)_xO(CF_2)_5O(CFCF_2O)_yCF$ (R1, R2, R2, R1)	0.20	-18
1		$R_1,R_2 = CF_3$ $x + y = 5$ (HFPO-based)		
	"	"	0.26	-40
		$R_1,R_2 = F$ $x + y = 5$ (TFEO-based)		
		"	0.23	-19
	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$R_1,R_2 = CF_3$ $x + y = 4$ (HFPO-based)		
2	"	"	0.28	-41
		$R_1,R_2 = F$ $x + y = 4$ (TFEO-based)		
	"	"	0.25	-23
		$R_1,R_2 = CF_3$ $x + y = 5$ (HFPO-based)		
	"	"	0.27	-35
3		$R_1=CF_3,R_2=F$ $x + y = 5$ (TFEO:HFPO-based)		
	"	"	0.26	-45
		$R_1,R_2 = F$ $x + y = 5$ (TFEO-based)		

TABLE V

HYDROLYSIS TEST AT 95% RELATIVE HUMIDITY AND 93°C(200°F)

Test Nr	R_f' / R_f	Hrs.	Infrared Absorption at 1740 cm^{-1}	(a) Original Tg-°C	Final Tg-°C	(b) Original η_{inh}-dl/g	Final η_{inh}-dl/g
1	$(CF_2)_2O(CF_2)_5O(CF_2)_2$ / $CF_2(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF_2$ x + y = 6 (TFEO-based)	364	Strong absorption after 48 hrs. as well as absorption at 1710cm^{-1}. Very strong absorption at 1710cm^{-1} after 70 hrs.	-52	-	0.24	-
2	$(CF_2)_2O(CF_2)_5O(CF_2)$ / $CF_2(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF_2$ x + y = 5 (TFEO-based)	364	Very strong absorption at 1710cm^{-1} after 170 hrs.	-45	-	0.26	-
3	$(CF_2)_2O(CF_2)_5O(CF_2)_2$ / $CF(OCF_2CF)_xO(CF_2)_5O(CFCF_2O)_yCF$ (CF_3 CF_3 CF_3 CF_3) x + y = 5 (HFPO-based)	654	Initial very weak absorption did not change upon exposure.	-23	-23	0.25	0.23
4	$(CF_2)_2O(CF_2)_2O(CF_2)_2O(CF_2)_5O(CF_2)_2$ / $CF(OCF_2CF)_xO(CF_2)_5O(CFCF_2O)_yCF$ (CF_3 CF_3 CF_3 CF_3) x + y = 5 (HFPO-based)	654	"	-34	-33	0.35	0.31
5	$(CF_2)_2O(CF_2)_5O(CF_2)_2$ / $CF(OCF_2CF_2)_xO(CF_2)_5O(CF_2CF_2O)_yCF$ (CF_3 CF_3) x + y = 5 (TFEO:HFPO-based)	1010	Initial very weak absorption increased very slightly after 330 hours. No additional increase with longer exposure.	-35	(c)	0.27	0.21
6	$(CF_2)_2O(CF_2)_5O(CF_2)_2$ / $CF(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF$ (CF_3 CF_3) (TFEO:HFPO-based)	768	Initial very weak absorption did not change upon exposure.	-45	-42	0.29	0.25

(a) Differential Scanning Calorimetry ($\Delta T = 20°C/min$).

(b) 0.2 g/dl, 25°C, HFIP.

(c) Insufficient sample.

and further confirmed the superior hydrolytic stability of the FEB polymers synthesized from the pure TFEO:HFPO-derived dithioimidate ester.

4. CONCLUSIONS

From the results presented in this report, it is concluded that high molecular weight, thermooxidatively and hydrolytically stable FEB polymers can be synthesized by the polycondensation of fluorocarbon ether bis(o-aminophenol) monomers with novel HFPO- or TFEO:HFPO-derived dithioimidate ester monomers. Because of their minimal HFPO content, the TFEO:HFPO-derived dithioimidate esters can be tailored to impart hydrolytic stability to the resultant polymer structures while minimizing undesirable, concomitant increases in Tg over the analogous TFEO-based FEB polymers.

Selection of dithioimidate ester monomer govern both the Tg and hydrolytic stability of the resultant FEB polymers. Lower Tg's are observed with increased fluorocarbon ether content and especially with increased TFEO content. Although somewhat higher than in the analogous TFEO-based polymers, the Tg's of the TFEO:HFPO-based FEB polymers are considerably lower than in HFPO-based polymers. Maximum hydrolytic stability and a minimum Tg of -48°C (-55°F) can be achieved through the use of a TFEO:HFPO-derived dithioimidate ester monomer prepared by an unambiguous synthetic route specifically selected to eliminate formation of undesirable structural isomers which can lead to sites of hydrolytic instability in the polymer backbone.

Based on the TGA and isothermal aging studies in air, long term use at temperatures approaching 260°C (500°F) is envisioned. The thermo-oxidative stability data coupled with the polymer Tg and hydrolytic stability data strongly indicate great potential for achieving a broader use temperature range than currently available in state-of-the-art elastomers. In accordance with the objective stated earlier, it appears likely that with additional research to improve curability, the FEB polymers will provide candidate materials for severe environment seal applications in advanced Air Force aircraft and cruise missles.

SECTION III

EXPERIMENTAL

1. PREPARATION OF SOLVENTS AND INTERMEDIATES

Hexafluoroisopropanol (HFIP) and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) obtained from Pierce Chemical Company and Dupont, respectively, were dried over magnesium sulfate and redistilled.

The HFPO- and TFEO:HFRO-derived fluorocarbon ether dinitriles were obtained from PCR, Inc., under Air Force Contract F33615-75-C-5075 (References 19 and 20). The α,ω-fluorocarbon ether iodoester, $I(CF_2CF_2O)_5CF(CF_3)CO_2CH_3$, was obtained from PCR, Inc., under Air Force Contract F33615-76-C-5019 (Reference 21).

2. PREPARATION OF MONOMERS

The requisite fluorocarbon ether bis(o-aminophenol) monomers had been prepared under earlier phases of the current effort (References 1-3, 5-7).

The following is a representative preparative procedure used in the syntheses of the HFPO- and TFEO:HFPO-derived dithiomidate ester monomers from the corresponding dinitriles supplied by PCR, Inc.

Synthesis of $H_5C_2S(HN=)CCF(CF_3)(OCF_2CF_2)_8OCF(CF_3)C(=NH)SC_2H_5$

The fluorocarbon ether dinitrile, $NCCF(CF_3)(OCF_2CF_2)_8OCF(CF_3)CN$, (20.4 g, 17 mmol), was added over a five-minute period to a vigorously stirred solution of one ml of dry triethylamine in 20 ml of ethanethiol. The temperature of the resultant two-phase reaction mixture was main-

tained at 35°C for 24 hours at which time the triethylamine and excess ethanethiol were distilled off. Distillation of the dark yellow residue yielded 17.1 g (81% yield) of viscous, water white monomer, bp 146-149°C/0.03 mm Hg.

Analysis: Calc'd: C, 23.65; H, 0.92; N, 2.12; S, 4.85.

Found: C, 23.75; H, 0.65; N, 2.01; S, 4.71.

Molecular weight (mass spectroscopy) Calc'd 1320; Found: 1320.

The preparative procedure for the synthesis of the TFEO:HFPO-derived dithioimidate ester monomer from $I(CF_2CF_2O)_5CF(CF_3)CO_2CH_3$ is as follows.

Synthesis of $H_5C_2S(HN=)CCF(CF_3)(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF(CF_3)C(=NH)SC_2H_5$

A mixture of the iodoester, $I(CF_2CF_2O)_5CF(CF_3)CO_2CH_3$, (65.2 g, 75 mmol), 40 mesh zinc (15.0 g, 234 mmol), and acetic anhydride (46.0 g, 45 mmol) in 130 ml of Freon 113 were heated to reflux temperature (ca 54°C) with stirring for three days. During the course of the reaction a white precipitate formed. The cooled reaction mixture was filtered and the filtrate washed with water and saturated sodium bicarbonate solution. The resultant Freon 113 solution of the unpurified diester was dried over anhydrous magnesium sulfate. Ammonia was then bubbled slowly through the solution at room temperature for five days. A small amount of precipitate that formed was then removed by filtration and the filtrate evaporated to dryness to yield an off-white solid. The combined precipitate and residue was recrystallized from chloroform to yield 40.7 g (75% yield) of the fluorocarbon ether diamide, mp 59.0-60.5°C. The infrared and nuclear

magnetic resonance spectra were consistent with the proposed structure.

Analysis: Calc'd: C, 21.56; H, 0.28; N, 1.93.

Found: C, 22.04; H, 0.24; N, 2.10.

The fluorocarbon ether diamide, $H_2NCOCF(CF_3)(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF(CF_3)CONH_2$, (38.0 g, 26 mmol) was thoroughly mixed with an excess (ca 100 g) of phosphorus pentoxide and heated under nitrogen to 210°C for six hours. The crude product was then distilled under reduced pressure while the temperature was gradually increased to 250°C. The crude distillate (25.6 g) was redistilled to give 21.8 g (58% yield) of the pure fluorocarbon ether dinitrile, bp 115-118°C/0.17 mm Hg. The infrared and nuclear magnetic resonance spectra were consistent with the proposed structure.

Analysis: Calc'd: C, 22.11; H, 0.00; N, 1.98.

Found: C, 22.38; H, 0.11; N, 1.96.

The fluorocarbon ether dinitrile, $NCCF(CF_3)(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF(CF_3)CN$, (21.8 g, 15 mmol) was added dropwise over a 30 minute period to a vigorously stirred solution of one ml of dry triethylamine in 20 ml of ethanethiol. Stirring was maintained at room temperature for two days at which time the excess ethanethiol and triethylamine were distilled over at atmospheric pressure. The clear yellow residue was then distilled to give 18.0 g (80% yield) of viscous, pale yellow monomer, bp 178-180°C/0.40 mm Hg. The infrared, nuclear magnetic resonance, and mass spectral data were consistent with the proposed structure.

Analysis: Calc'd: C, 23.45; H, 0.78; N, 1.82; S, 4.17.

Found: C, 23.61; H, 0.58; N, 1.81; S, 4.31.

3. PREPARATION OF POLYMERS

A typical synthetic procedure for the polymers is as follows:

TFEO:HFPO-based FEB Polymer (Trial Nr. 5)

The fluorocarbon ether dithioimidate ester monomer, $H_5C_2S(HN=)CCF(CF_3)(OCF_2CF_2)_4O(CF_2)_4O(CF_2CF_2O)_4CF(CF_3)C(=NH)SC_2H_5$, (1.09 g, 0.66 mmol) and 1,11-bis(3-amino-4-hydroxyphenyl)perfluoro-3,9-dioxaundecane (0.463 g, 0.66 mmol) were dissolved in 3 ml of HFIP to give a clear, pale yellow solution. Glacial acetic acid (0.22 g, 3.64 mmol) was added and the clear polymerization mixture stirred under nitrogen at 55°C for 672 hours. The resultant viscous, amber solution was slowly added to 100 ml of methanol and the precipitated polymer was dried. It was redissolved in 15 ml of Freon 113 and the solution filtered. Reduction in solution volume to 5 ml followed by precipitation in methanol yielded a swollen, sticky polymer which was dried at 100°C and 0.01 mm Hg for 16 hours to give 1.10 g (80% yield) of amber gum (inherent viscosity = 0.29 dl/g in HFIP at 25°C).

Analysis: Calc'd: C, 27.19; H, 0.29; N, 1.35.

Found: C, 27.52; H, 0.02; N, 1.45.

REFERENCES

1. R. C. Evers, Air Force Materials Laboratory, AFML-TR-75-11 (August 1977).

2. R. C. Evers, U. S. Patent Nr. 4,005,142 (1977).

3. R. C. Evers, U. S. Patent Nr. 3,994,861 (1976).

4. R. C. Evers, J. Poly. Sci., Poly. Chem. Ed., 16, 2818 (1978).

5. R. C. Evers, J. Poly. Sci., Poly. Chem. Ed., 16, 2833 (1978).

6. R. C. Evers, Air Force Materials Laboratory, AFML-TR-74-66 (June 1974).

7. R. C. Evers, Polymer Preprints, 15 (1), 685 (1974).

8. R. C. Evers, U. S. Patent Nr. 3,903,166 (1975).

9. R. C. Evers, U. S. Patent Nr. 3,846,376 (1974).

10. N. L. Madison and C. D. Burton, Air Force Materials Laboratory, AFML-TR-67-261, Part I (September 1967).

11. N. L. Madison and C. D. Burton, Air Force Materials Laboratory, AFML-TR-67-261, Part II (December 1968).

12. N. L. Madison and C. D. Burton, Air Force Materials Laboratory, AFML-TR-67-261, Part III (October 1969).

13. N. L. Madison, C. D. Burton, and R. W. Anderson, Air Force Materials Laboratory, AFML-TR-67-261, Part IV (February 1971).

14. C. D. Burton and N. L. Madison, U. S. Patent Nr. 3,560,438 (1971).

15. C. D. Burton and N. L. Madison, U. S. Patent Nr. 3,564,003 (1971).

16. C. D. Burton and N. L. Madison, U. S. Patent Nr. 3,565,908 (1971).

17. C. Tamborski and G. J. Moore, Air Force Materials Laboratory, AFML-TR-76-104 (September 1976).

18. E. J. Soloski, G. J. Moore, and C. Tamborski, J. Fluorine Chem., 8, 295 (1976).

19. T. Psarras, Air Force Materials Laboratory, AFML-TR-77-99 (July 1977).

20. T. Psarras, Air Force Materials Laboratory, AFML-TR-76-144 (August 1976).

21. K. Baucom, Air Force Materials Laboratory, AFML-TR-77-223 (December 1977).

22. L. J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd Edition, Metheun and Co., Ltd., London (1958).

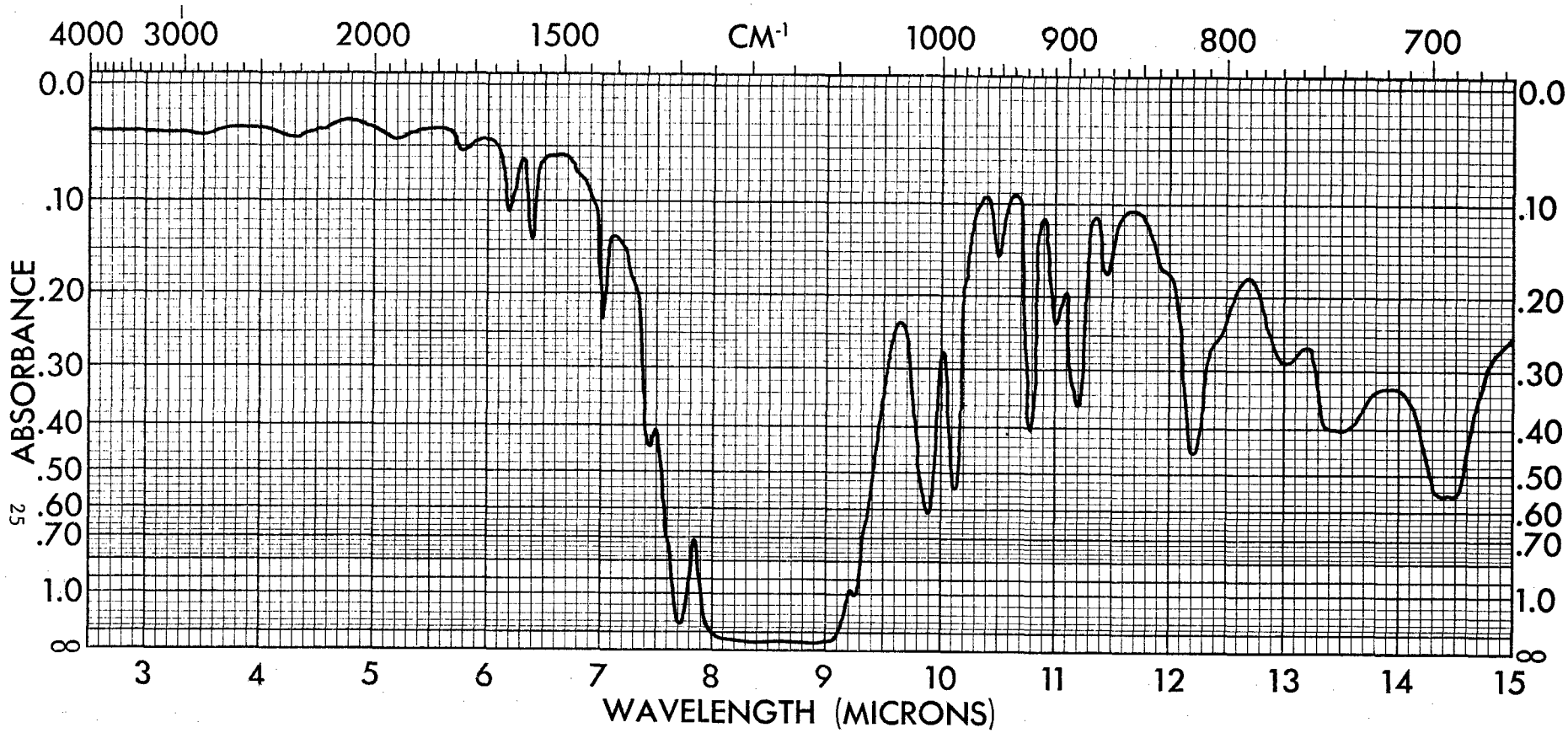
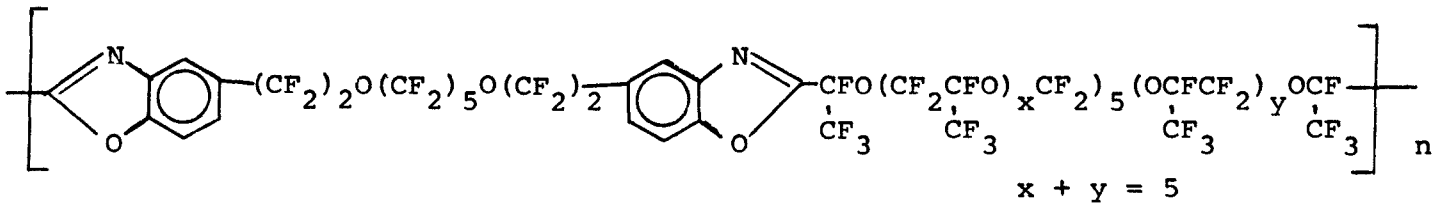


Figure 1. Infrared Spectrum of TFEO:HFPO-Based Polymer (Trial Nr 5)(Film)



x + y = 5

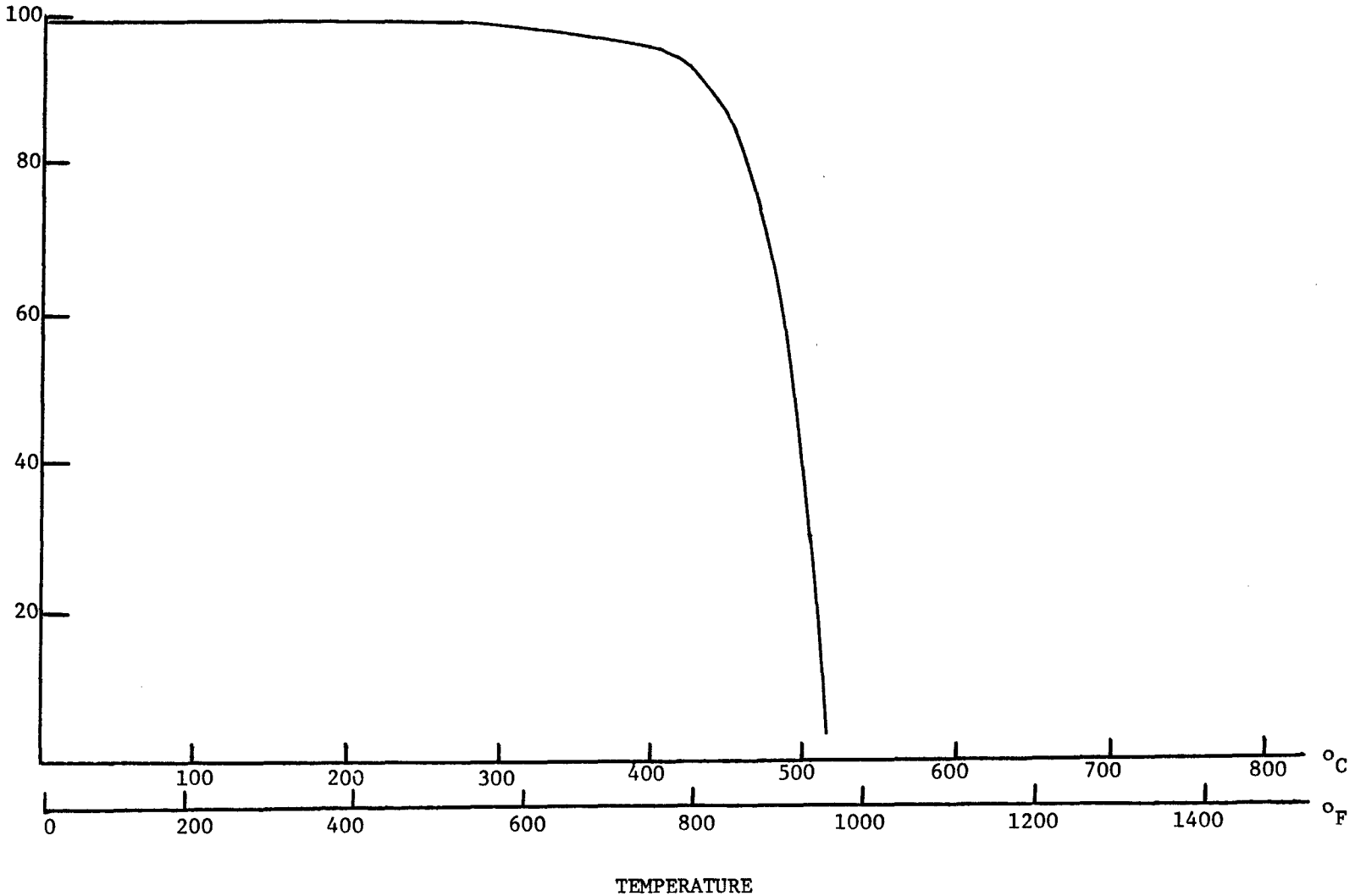


Figure 2. TGA Curve of HFPO-Based Polymer (Trial Nr 4) in Air ($\Delta T = 20^{o}C/min$)

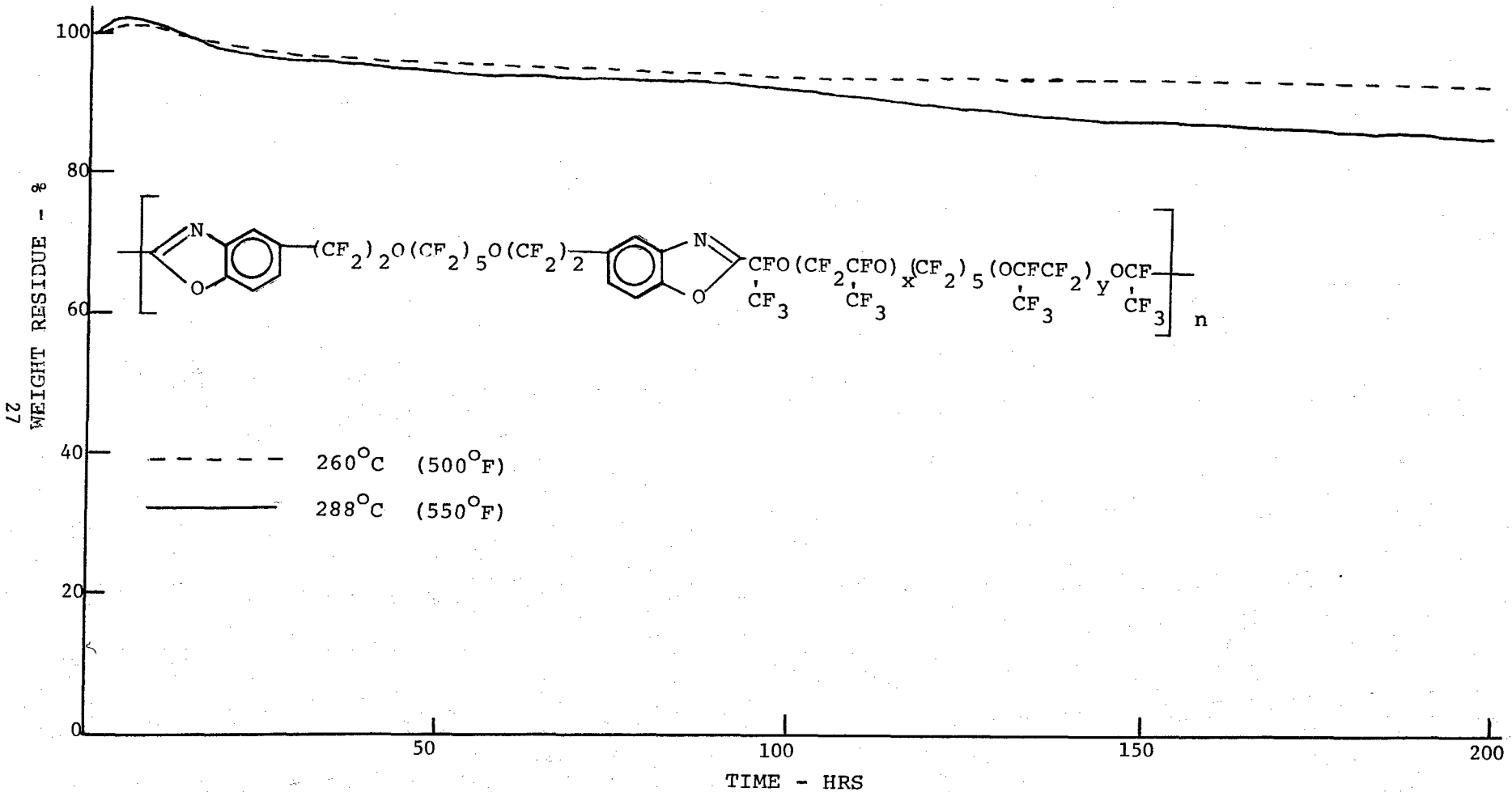


Figure 3. Isothermal Aging Curves of HFPO-Based Polymer (Trial Nr 4) in Air

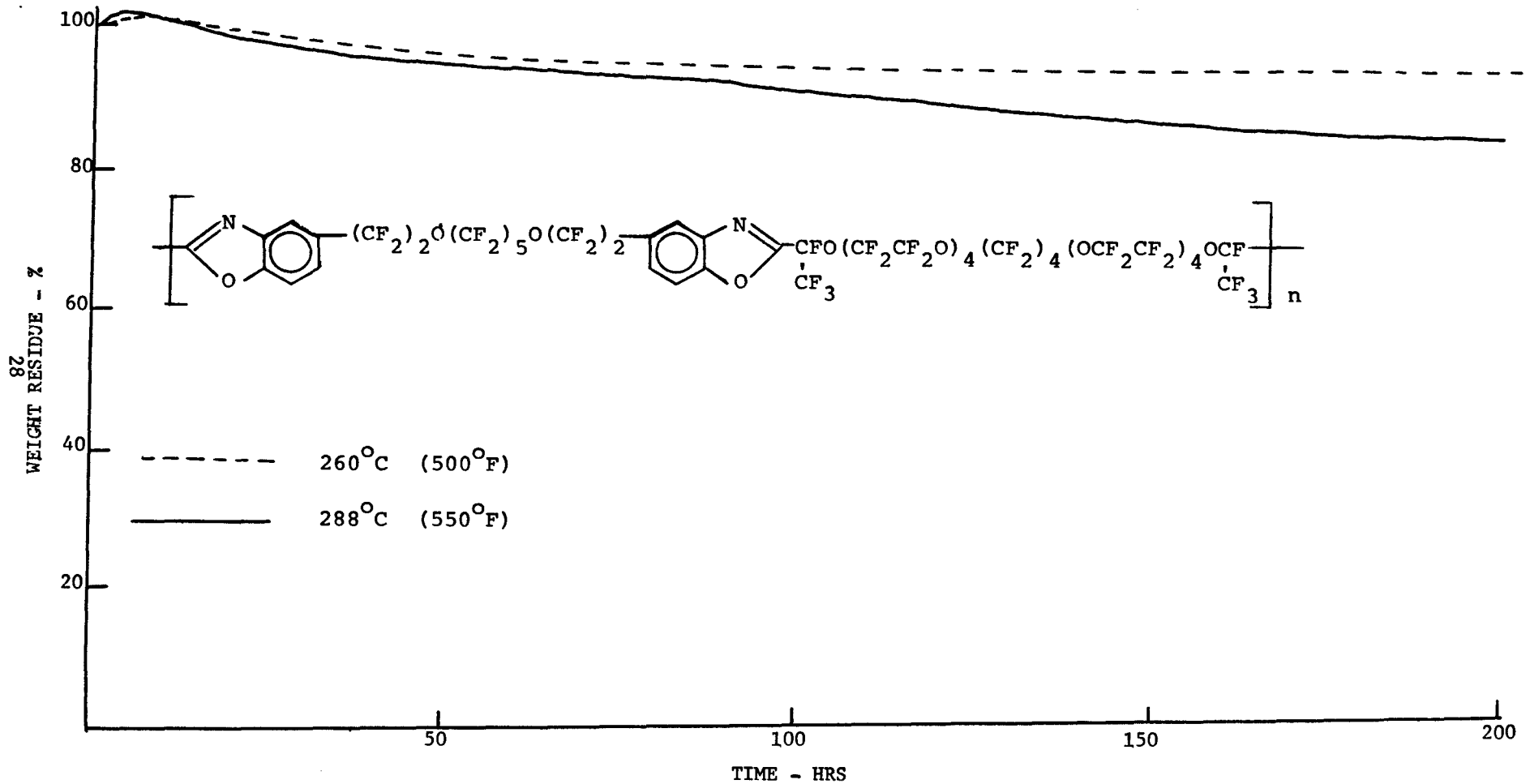
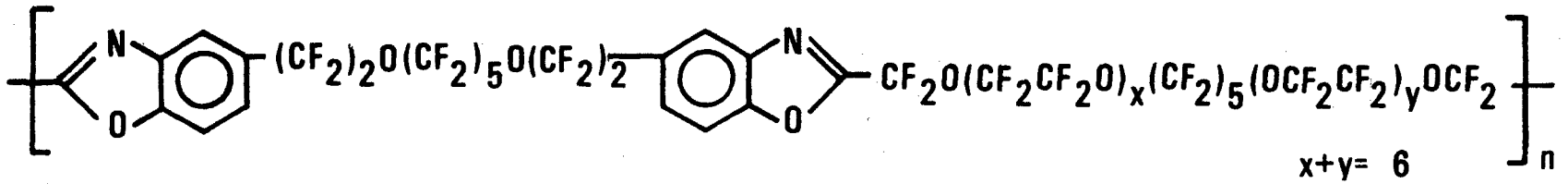


Figure 4. Isothermal Aging Curves of TFEO:HFPO-Based Polymer (Trial Nr 5) in Air



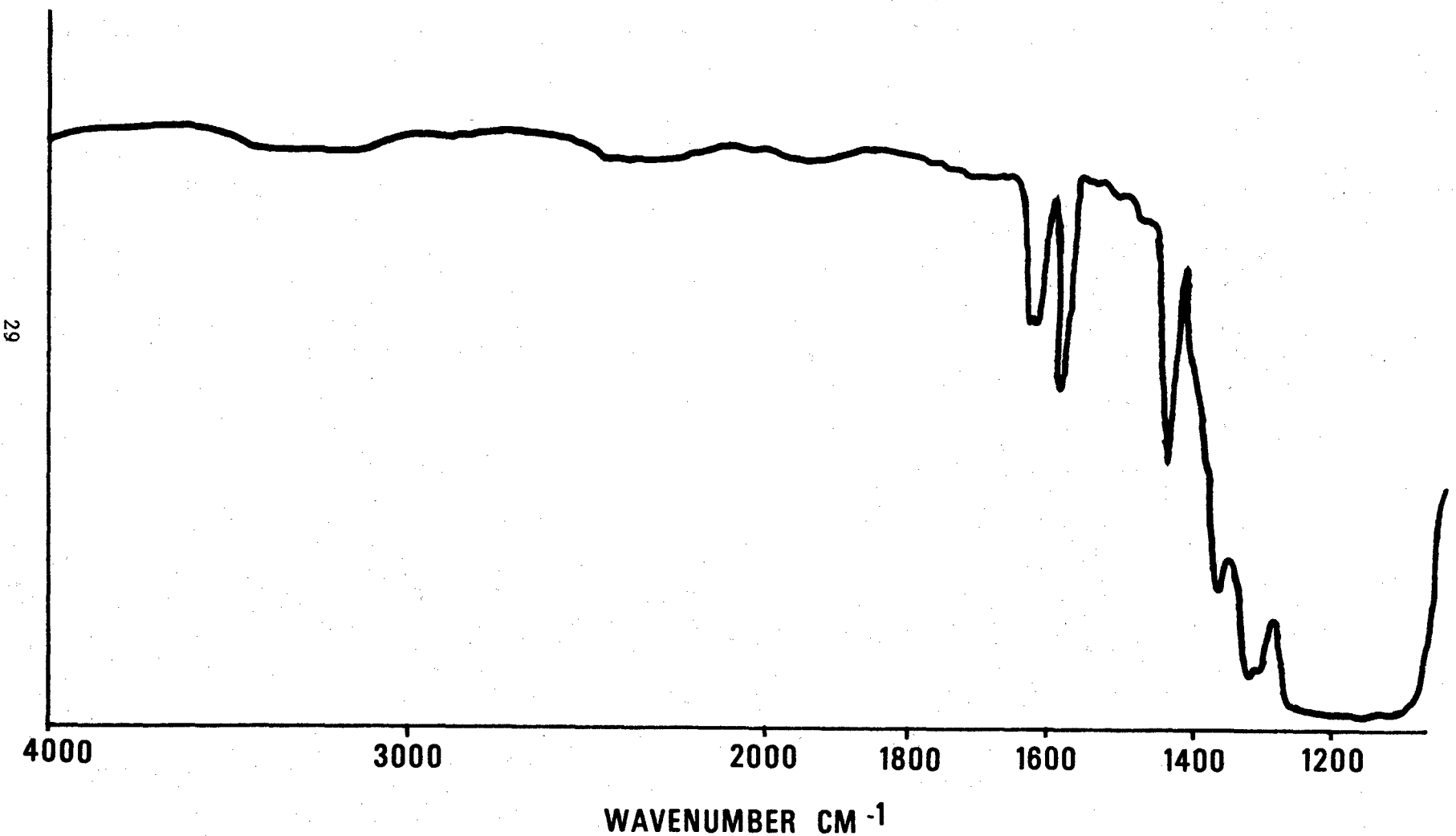


Figure 5. Infrared Spectrum of TFEO-Based Polymer (Film)

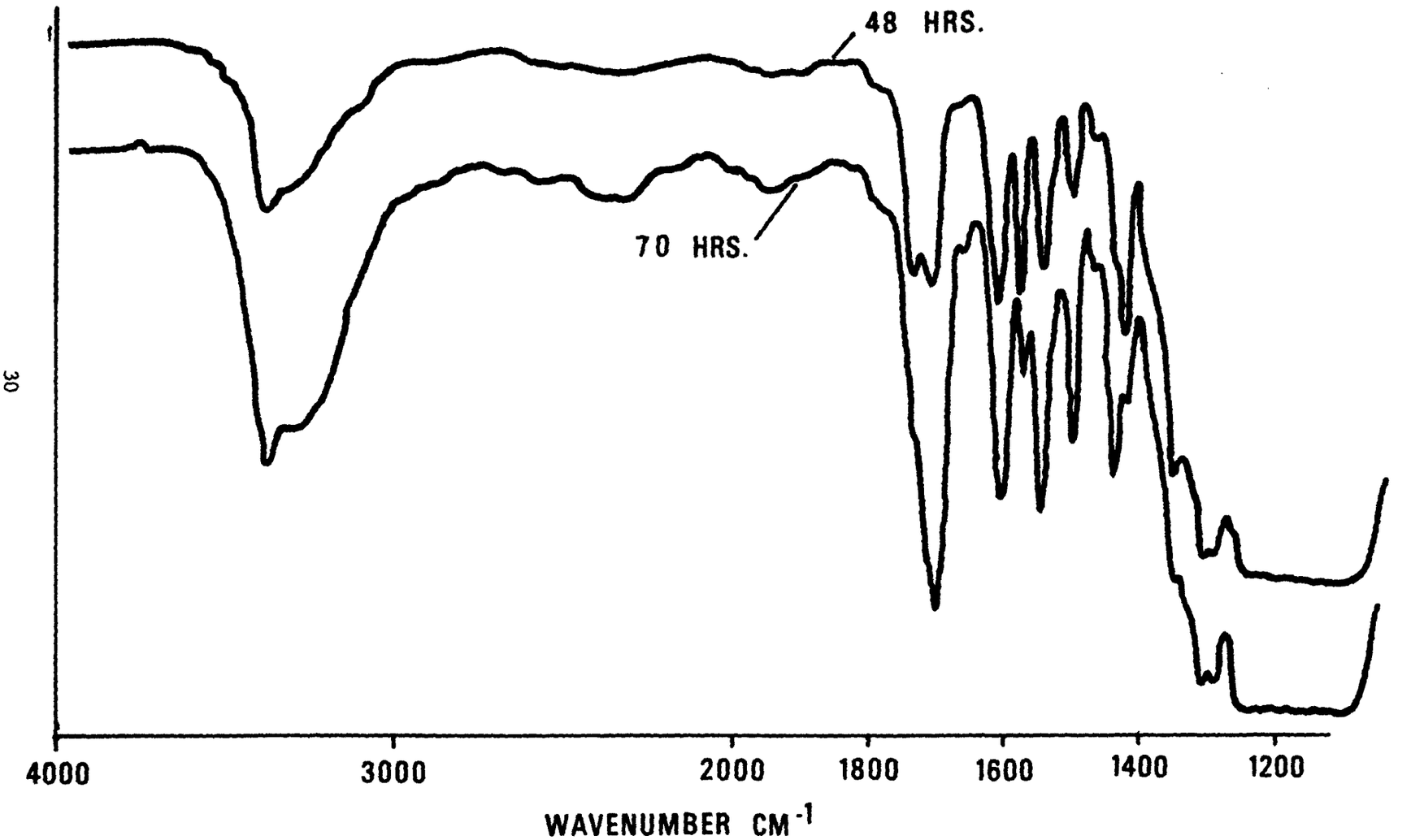


Figure 6. Infrared Spectra of TFEO-Based Polymer After Exposure to 95% R.H., 93°C(200°F) Environment (Film)

*U.S.Government Printing Office: 1979 — 657-084/376